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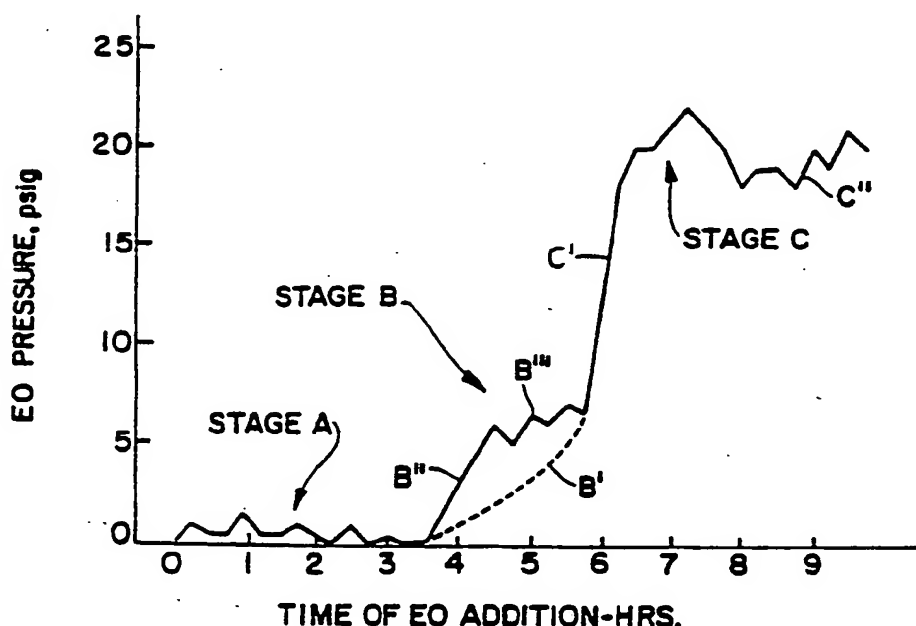
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C07C 43/11, 43/20, 67/24 C07C 67/26, 69/76, C09F 5/08		A1	(11) International Publication Number: WO 90/14327 (43) International Publication Date: 29 November 1990 (29.11.90)
(21) International Application Number: PCT/US90/02909 (22) International Filing Date: 23 May 1990 (23.05.90) (30) Priority data: 357,155 26 May 1989 (26.05.89) US (71) Applicant: GAF CHEMICALS CORPORATION [US/ US]; 1361 Alps Road, Wayne, NJ 07470 (US). (72) Inventors: MERRIFIELD, James, H. ; 29 Kings Road, Landing, NJ 07850 (US). HASHEM, Mohamed, M. ; 100 Magnolia Place, Wayne, NJ 07470 (US). LOGIN, Robert, B. ; 137 Page Drive, Oakland, NJ 07436 (US). (74) Agent: LAMBIRIS, Elias, J.; Morgan & Finnegan, 345 Park Avenue, New York, NY 10154 (US).			(81) Designated States: AT (European patent), AU, BE (Euro- pean patent), BR, CH (European patent), DE (European patent)*, DK, DK (European patent), ES (European pa- tent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent). Published With international search report.

(54) Title: LIQUID SURFACTANT POLYMERS OF TETRAHYDROFURAN AND ETHYLENE OXIDE



(57) Abstract

Liquid surfactant polymer products of tetrahydrofuran and ethylene oxide, and process for making the same, are provided herein. The polymers comprise a hydrophobic central segment, transition copolymer segments extending outwardly from the central segment characterized by a continuously increasing EO mer unit content relative to the THF mer units therein, and hydrophilic terminal segments of substantially EO mer units.

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LIQUID SURFACTANT POLYMERS OF
TETRAHYDROFURAN AND ETHYLENE OXIDE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to copolymers of tetrahydrofuran (THF) and ethylene oxide (EO), and, more particularly, to liquid surfactant polymers of THF and EO having a wide range of molecular weight and monomer content.

2. Description of the Prior Art

Surfactants based upon copolymers of THF and EO are disclosed as alternatives to nonionic surfactants. Block copolymers of these monomers have a well-defined hydrophilic and hydrophobic structure and exhibit useful surface active properties. Unfortunately, block copolymers are pastes or solids at ambient temperatures which makes them very difficult to handle.

Kuwamura et al., in the J. of Am. Oil Chem. Soc. 51, 29-34 (Feb., 1971), described block copolymers of ethylene oxide and polyoxytetramethylene glycols prepared by cationic polymerization of tetrahydrofuran as being solids with surfactant properties albeit with rather high pour points and poor defoaming action.

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Grief et al., in U.S. Patent 4,038,296, described modified block copolymers of THF and EO which included a long chain (C_8-C_{21}) alcohol. Their product was defined as R-X in which the hydrophobic portion, R, was provided by the long chain hydrocarbon radical of the alcohol, and the hydrophilic end, X, was provided by the reaction product of the THF and EO monomers. These copolymers were disclosed to be useful as textile auxiliaries and surfactants.

Random copolymers of THF and EO, on the other hand, are liquids, but they do not exhibit the effective surface active properties which are characteristic of the corresponding block copolymers. Random copolymers of THF and EO are produced by copolymerizing a mixture of the monomers, or by adding one monomer to the other at a substantially constant feed rate.

Pruckmayr, in U.S. Patent 4,139,567, for example, described the preparation of random copolymers of THF and EO using acidic resins as catalysts for the polymerization. The disclosed process involved precharging THF and the resin catalyst and then slowly bubbling in gaseous EO at a substantially constant feed rate over a two-hour period while holding the reaction mixture at 25°C.

Langdon et al., in U.S. Patent 4,183,821, disclosed random-block copolymers of THF and EO which were prepared by a two-stage process. The first stage of the process comprised forming the random hydrophobic portion of the polymer by reacting a mixture of THF and EO in the presence of a Lewis acid catalyst. The hydrophobic segment then was capped with a hydrophilic block of ethylene oxide units by a base-catalyzed reaction with EO. The product was a random-block copolymer characterized by an abrupt break between its hydrophobic segment and its hydrophilic cap. Demulsifying properties were observed for such polymers but it was not apparent that they had effective surfactant properties.

Knopf et al., in U.S. Patent 4,195,167, disclosed the formation of gradient copolymers of ethylene oxide and propylene oxide which were considered as intermediate between block and random copolymers. Such gradient copolymers of ethylene oxide and propylene oxide were produced by a process in which one of the premixed concentrations of the primary and secondary polymerizable monomer feed compositions was continuously changed during the polymerization. However, a suitable process for preparing liquid copolymers of tetrahydrofuran and ethylene oxide having effective surfactant properties was not disclosed.

The following references are also of interest in this field: U.S. Patents: 3,133,095; 3,194,772; 3,254,056; 3,344,088; 3,359,332; 3,425,999; 3,644,567; 3,834,935; 4,065,520; 4,118,326; 4,198,464; 4,259,405; and 4,299,993; Brit. Pat. No. 854,958; Japan Patent Announcement No. 213-1977; and an article by Murbach, W. and Adicoff, A. in Ind. & Eng. Chem., 52, 7725 (1960).

None of the above cited references, however, disclose, describe or suggest a suitable method for preparing copolymers of THF and EO which are liquids at ambient temperatures, and which exhibit effective surfactant properties, i.e. surface tension reduction, low pour points, good defoaming action, and effective lubricity, and wherein such copolymers exhibit these advantageous surfactant properties over a wide range of molecular weights and monomer content.

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Accordingly, an object of the invention is to provide liquid surfactant polymers of THF and EO which are effective surfactants over a wide molecular weight range, and, particularly, which exhibit substantial surface tension reduction, low foaming, low pour points, and useful lubricity surfactant properties.

Another object of the invention is to provide a process for making such liquid surfactant polymers.

These and other objects and features of the invention will be made apparent from the following summary and description of the invention.

SUMMARY OF THE INVENTION

The present invention provides a liquid surfactant polymer product which is substantially a copolymer of THF and EO monomers (mer) units. The polymer structure comprises:

- (1) a hydrophobic central THF-EO copolymer segment containing predominately THF mer units,
- (2) transition THF-EO copolymer segments extending outwardly from the central copolymer segment characterized by a continuously increasing EO mer unit content relative to the THF mer units therein, and
- (3) hydrophilic termini polymer segments of substantially EO mer units.

The liquid surfactant polymers of the invention have useful surfactant properties, including surface tension reduction, low foaming, low pour points, and effective lubricity, within a polymer molecular weight range of about 500 to 10,000, and, preferably, about 1,500 to 5,000.

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The invention also provides a multi-stage process for making the liquid surfactant polymer product described herein. In this process, predetermined amounts of EO are added successively to a charge of THF at selected rates. Polymerization is carried out in a predetermined manner at the various stages of the process to form the desired segments of the polymer.

BRIEF DESCRIPTION OF THE DRAWING

The FIGURE is a graphical illustration of the process of the invention, showing the rate of addition of EO to a charge of THF at each stage of the process.

DETAILED DESCRIPTION OF THE INVENTION

As illustrated in the FIGURE, a 3-stage process is provided for preparing the liquid surfactant polymer product of the invention. During the several stages of the process, three segments of the polymer are provided, each with a predetermined monomer content.

CHARGE

The process is carried out by first charging a reactor with THF monomer reactant and a small amount of a starter compound for the polymerization. The starter will enable linear polymerization of the monomers in one or more directions, depending upon the number of reactive hydrogens in the starter. Suitably, the starter is added in an amount of about 0.1-10 mol % of all monomers present in the reaction. Representative starter compounds include

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monohydric or polyhydric alcohols, alcohol, such as butanol, ethylene glycol, butanediol, decanediol, glycerol, pentaerythritol, bis-phenol A, nonyl phenol, polyethylene glycol, polypropylene glycol, polytetrahydrofuran, and the like, and monobasic and polybasic acids, such as acetic acid, stearic acid, succinic acid, oxalic acid, gluaric acid, benzoic acid, and the like, although others known in the art may be used as well, including primary and secondary amines, hydroxyl amines, and water. The reactor is then sealed, purged with nitrogen, and warmed to a reaction temperature. Suitably, the reaction temperature is set above the boiling point of EO (10°C.) and below about 80°C., preferably about 45°-60°C. A polymerization catalyst then is added, such as a Lewis acid, of which BF_3 -etherate is one example.

HYDROPHOBIC CENTRAL SEGMENT

The EO monomer reactant then is introduced slowly into the charged reactor at a low EO pressure, as shown by stage A in the FIGURE. Suitably, the EO pressure does not exceed about 2 psig, and preferably less than 1 psig. During introduction of the EO monomer, in this stage of the process, the reaction temperature gradually increases, generally, from about 45°C. to about 50°-60°C. Copolymerization is thereby effected between the charged THF reactant and the small amount of added EO to form the hydrophobic central segment of the polymer which contains predominately THF mer units. The EO addition is continued until about 1/2 to 2/3 of the THF charge is consumed. This segment preferably includes, relatively, about 10-20 THF mer units to about 2-4 EO mer units.

TRANSITION COPOLYMER SEGMENTS

Substantially all of the remaining THF reactant then is copolymerized with newly added EO, in stage B, to form the transition THF-EO copolymer segments of the polymer which extend outwardly from the central copolymer segment. These transition segments are characterized by a continuously increasing EO mer unit content relative to the THF mer units therein.

To form the transition segments, the rate of EO addition is increased slowly, for example, up to about 5-8 psig., over a period of about an hour, as shown in the graph. The EO addition during this stage may be carried out in one step, shown as step B', or, in two successive steps, B'' and B'''. In the latter pathways, the EO reaction pressure is increased to the desired level (during step B'') and then it is held constant (during step B''') for a given period of time at the reaction temperature. At the conclusion of stage B, substantially all of the remaining THF charge is consumed to provide the transition segments. Generally, the transition segments preferably include, relatively, about 4-15 THF mer units to about 4-30 EO mer units. The EO mer unit content in these segments continuously increase outwardly and away from the central segment.

HYDROPHILIC TERMINI SEGMENTS

Upon determination by analysis that substantially all the THF charge has been consumed in stage B, the transition segments then are capped with hydrophilic EO polymer termini segments during stage C of the process. These caps are provided by feeding EO into the reactor at an increased rate. Generally, stage C also is carried out in two steps, namely, step C', in which the EO pressure is

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increased substantially, e.g. to about 20 psig, and step C'', wherein the remainder of the EO reactant is added. The termini segments preferably contain about 3-40 EO mer units, although lower and higher amounts also may be present.

ISOLATION OF PRODUCT

The reactor then is purged with nitrogen, cooled, e.g. to about 35°C., and the reaction product is discharged. The reaction then is terminated by complexing the catalyst for example, with a diatomaceous earth or by ion-exchange. The reaction product mixture then is stirred, filtered and vacuum stripped of volatiles. The polymer product obtained thereby is a clear, colorless viscous liquid, containing, relatively, about 14-35 THF mer units to about 9-100 EO mer units.

The molecular weight of the polymer product suitably is about 500 to about 10,000, and preferably about 1,500 to 5,000. The product exhibits excellent surfactant properties of substantial surface tension reduction, low foaming, low pour points, and effective lubricity.

The invention will now be described by reference to the following examples.

EXAMPLE 1

A dry, stainless steel reactor was charged with 256 g. (2.85 moles) of butanediol and 8,616 g. (119 moles) of THF (maximum water content of 0.01%). The reactor was sealed, purged with nitrogen and warmed to 45°C. Then a solution of 10 g. of boron trifluoride-etherate in 15 ml. of diethyl ether was added.

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Ethylene oxide (3,258 g., 74 moles) then was slowly pumped into the reactor at a slow rate such that the reaction pressure was about 1 psig. This pressure corresponds to an EO flow rate of approximately 300 g. of EO per hour. During the addition, the reaction temperature gradually increased to about 50°-60°C. After 4 hours, approximately 1200 g. of EO had been added for copolymerization with the charged THF reactant.

The rate of EO addition then was slowly increased during about an hour so that a reaction pressure of about 5-8 psig was reached. Thereafter, the reaction mixture is maintained at this pressure for 3 hours while the reaction temperature was controlled at 60°C.

The rate of EO addition then was increased within a period of about 15 minutes until the reaction pressure reached about 20 psig. Meanwhile, the reaction temperature was controlled at 60°C. The remaining EO reactant then was added for about 2-1/2 hours. Then the mixture was stored for an hour.

The reaction product was then purged with nitrogen for 15 minutes, cooled to 35°C., and discharged. Magnasol (50 g.) was added and the mixture was stirred for 2 hours at 65°C. The Magnasol was removed by filtration and the product was vacuum stripped at 60°C. with a slight nitrogen sparge. The product was a clear, colorless, viscous fluid.

EXAMPLES 2 - 10

The procedure of Example 1 was followed using different amounts of the THF monomer reactant, initiator and catalyst, and EO rate of addition. The products obtained were liquid surfactant polymers of varying molecular weights having effective surfactant and other physical properties.

The process parameters of Examples 1-10 are shown in Tables 1 and 2 below.

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TABLE 1

PREPARATION OF LIQUID SURFACTANT THF-EO POLYMERS OF INVENTION

Ex. No.	THF (g)	Starter (g)	BF ₃ Etherate Catalyst (g)	Amounts (g) and Times of EO		Total EO Added (g) of Polymer	Molar Ratios of Components
				Stage A	Stage B		
				Stage A	Stage B	Stage C	
1	8616	Butanediol (256)	10	1200(4)	1500(3)	55(2.5)	3258
2	1008	Butanediol (90)	2.5	300(3.5)	300(2)	400(6)	1012
3	1632	Butanediol (135)	2.5	250(4)	250(3)	140(1)	640
4	648	Butanediol (90)	2.5	250(3)	250(2)	150(5)	651
5	5040	Butanediol (225)	2.5	1500(5)	1500(3)	4502(8)	7502
6	1314	Glycerol (55)	2.5	250(3)	200(3)	183(3)	633
7	1260	Glycerol (46)	2.5	350(4)	300(4)	604(6)	1254
8	958	Butanol (70)	2.5	200(3)	200(3)	1147(8)	1547
9	1260	Butanol (37)	2.5	300(4)	300(3)	720(8)	1320
10	982	Decanediol (113)	2.5	200(3)	300(3)	951(7)	1451

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The molecular weights, surfactant and other physical properties of the polymers of the invention are shown in Table 2 below.

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TABLE 2

PROPERTIES OF LIQUID SURFACTANT THF-EO POLYMERS OF INVENTION

Ex. No.	Mol. Viscosity		Foam Ht. (mm)	Pour Point (°C.)	Cloud Point (°C.)	Lubricity (psi)	Surface Tension (dynes)		
	Wt.	(cps)					0.1	0.01	0.001
1	3750	2100	5	-4	11-14	3180	0.1	0.01	0.001
2	1940	950	10	-22	24-27	1980	38.9	42.1	45.1
3	1360	380	0	-40	20-24		41.0	43.5	45.8
4	1230	420	20	-34	40-43		38.5	40.5	43.0
5	4800	9100	30	-2	35-38		39.9	43.9	48.9
6	3725	4000	15	-2	11-12	3220	42.2	44.1	49.2
7	4870	14000	30	0	42-44	2200	49.7	52.1	55.6
8	2525	1275	10	-20	30-35		39.8	41.5	50.0
9	5000	8920	40	-2	25-28		40.1	41.5	49.8
10	3760	540	20	-30	23-25		37.1	39.4	46.0

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Mol. wt. - Determined by OH number

Viscosity - Brookfield viscosity at 26°C.

Foam Ht. - Ross-Miles method at room temperature - 0.1% solution

Cloud Point - 1% solution in water

Lubricity - Falex test, apparent gage load at failure, neat

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The results in Table 2 show that the liquid surfactant polymers of the invention have excellent surfactant properties, as evidenced by the substantial surface tension reduction. In addition, these surfactants exhibit low foaming, low pour point and excellent lubricity properties.

Although the invention has been described with reference to certain embodiments thereof, it will be understood that changes and modifications may be made which are within the skill of the art.

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WHAT IS CLAIMED IS:

1. A liquid surfactant polymer product consisting essentially of:

(a) a hydrophobic central THF-EO copolymer segment containing predominately THF mer units,

(b) transition THF-EO copolymer segments extending outwardly from said central copolymer segment characterized by a continuously increasing EO mer unit content relative to the THF mer units therein, and

(c) hydrophilic termini polymer segments of substantially EO mer units.

2. A liquid surfactant polymer product according to claim 1 wherein (a) includes, relatively, about 10-20 THF mer units to about 2-4 EO mer units; (b) includes, relatively, about 4-15 THF mer units to about 4-30 EO units, and (c) includes about 3-40 EO mer units.

3. A liquid surfactant polymer product according to claim 2 wherein the polymer includes, relatively, about 14-35 THF mer units to about 9-100 EO mer units.

4. A liquid surfactant polymer product according to claim 1 having a molecular weight of about 500 to about 10,000.

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5. A liquid surfactant polymer product according to claim 4 having a molecular weight of about 1,500 to about 5,000.
6. A liquid surfactant polymer product according to claim 1 wherein (a) segment includes a starter compound.
7. A liquid surfactant polymer product according to claim 6 wherein said starter compound is selected from a monohydric or polyhydric alcohol and a monobasic or polybasic acid.
8. A liquid surfactant polymer product according to claim 7 wherein said starter is butanediol, glycerol, butanol or decanediol.
9. A liquid surfactant polymer product according to claim 1 which is a colorless viscous liquid.
10. A liquid surfactant polymer product according to claim 1 which exhibit substantial surface tension reduction, low foaming, a low pour point, and good lubricity properties.

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11. A process for making the liquid surfactant polymer product of claim 1 which comprises:

(a) copolymerizing a charge of THF with a predetermined amount of EO to form a hydrophobic central copolymer segment containing predominately THF mer units,

(b) copolymerizing substantially the remainder of the THF charge with an increased amount of EO to form transition copolymer segments extending outwardly from the central copolymer segment and characterized by a continuously increasing EO mer unit content relative to the THF mer units therein, and

(c) forming hydrophilic termini polymer segments containing substantially EO mer units.

12. A process according to claim 11 wherein step (b) is carried out with an increasing amount of EO monomer reactant.

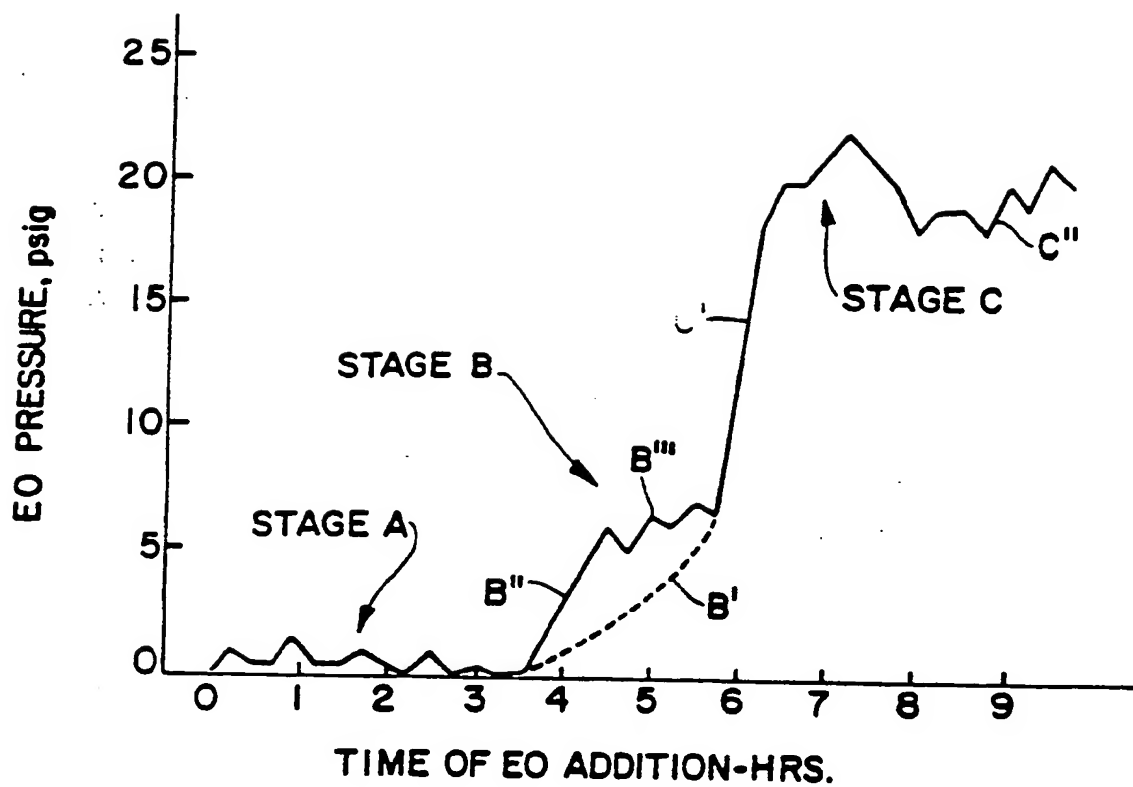
13. A process according to claim 11 wherein step (b) is carried out by increasing the amount of EO monomer reactant and then holding at a given level for a predetermined period.

14. A process according to claim 11 wherein step (a) is carried out in the presence of a starter compound.

15. A process according to claim 14 wherein said starter compound is selected from a monohydric or polyhydric alcohol and a monobasic or polybasic acid.

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FIGURE

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/02909

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
 IPC (5) : C07C 43/11, 43/20, 67/24, 67/26, 69/76; C09F 5/08
 U.S. Cl : 568/608, 609, 617; 260/410.6; 560/112, 200, 240

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System	Classification Symbols
U.S.	568/608, 609, 617; 260/410.6; 560/112, 200, 240

Documentation Searched other than Minimum Documentation
 to the Extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US, A 3,425,999 Published 04 February 1969 (AXELROOD ET AL)	1-10
Y	US, A 4,038,296 Published 26 July 1977 (GREIF ET AL)	1-15
Y	US, A 4,183,821 Published 15 January 1980 (LANGDON ET AL)	1-15
Y	US, A 4,299,993 Published 10 November 1981 (BETHEA ET AL)	1-15
Y	US, A 4,371,713 Published 01 February 1983 (MATSUMOTO ET AL)	1-15
Y	US, A 4,728,722 Published 01 March 1988 (MUELLER)	1-15

^{*} Special categories of cited documents: ¹⁰

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IV. CERTIFICATION

Date of the Actual Completion of the International Search

16 July 1990

Date of Mailing of this International Search Report

23 AUG 1990

International Searching Authority

ISA/US

Signature of Authorized Officer

For HOWARD T. MARS NGUYEN NSCC-HO INTERNATIONAL DIVISION

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	US,A	4,564,671 (MUELLER)	Published	14 January 1986	1-15
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V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____, because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

3. ☐ Claim numbers _____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ²

This International Searching Authority found multiple inventions in this international application as follows:

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2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

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